



## Degradable polyurethane based on star-shaped polyester polyols (trimethylolpropane and $\epsilon$ -caprolactone) for marine antifouling

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### ABSTRACT

The star-shaped polyester polyols based on initiators (trimethylolpropane or pentaerythritol) and  $\epsilon$ -caprolactone were prepared by polycondensation reaction. The degradable polyurethane (PU) films were prepared by mixing star-shaped polyester polyols and crosslinker agent (hexamethylene diisocyanate trimer). The hydrolytic degradation and water absorption experiments demonstrated that the PU films could erode in artificial sea water, which were controlled by varying the ratios of  $\epsilon$ -caprolactone/trimethylolpropane and the arm number of star-shaped polyester polyols. The mechanical properties of PU films and coatings increased with decreasing the ratios of  $\epsilon$ -caprolactone/trimethylolpropane and increasing the arm number of star-shaped polyester polyols. The surfaces of PU films and coatings kept eroding, which were revealed by scanning electron microscopy. The copper ion release rates from PU coatings reached steady state at about 31 days. The marine field tests of PU coatings demonstrated that the degradable PU coatings based on star-shaped polyester polyols were effective coatings for marine antifouling.

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### 1. Introduction

From the dawn of navigation, marine biofouling has been regarded as a serious problem. Marine antifouling paints, which protect ship hulls from biofouling by releasing booster biocides in a controlled manner, are the most reliable way to prevent biofouling [1–5]. The self-polishing triorganotin coatings have been the most effective ones until they were banned because of the high toxicity of triorganotin compounds [6]. Those environmental concerns lead to development of triorganotin-free coatings [7,8]. However, cuprous oxide is a main component of the tin-free booster biocides for marine antifouling at present, and its benefits as an antifouling booster biocide currently outweigh its environmental risk [9]. The self-polishing acrylate antifouling paints containing copper and other booster biocides, designed for the same reaction mechanism with sea water as the self-polishing triorganotin coatings, are

the main commercial products for marine antifouling [10]. Nevertheless, the self-polishing acrylate antifouling paints show poor resistance to cracks and peelings [11]. Most of the conventional self-polishing acrylate resins are predominantly thermoplastic, and low molecular-weight, linear polymers [12]. Despite their generally good properties for ordinary marine antifouling, lack of cross-linking ability in thermoplastic self-polishing acrylate resins makes them unsuitable for applications requiring higher mechanical properties [13]. Furthermore, the new offshore enterprises related to gas and oil industry have been creating new deep-sea substrata (platforms and vessels), which render the establishment of new biofouling communities as a challenge for researchers [11–14]. The deep-sea environment, high hydrostatic pressure and low water temperature, is very different from that of the sea at the surface, and the low adhesion strength of the self-polishing acrylate antifouling paints limits their applications in deep-sea substrata. To meet these demanding requirements, marine antifouling paints need superior mechanical properties and effective antifouling.

In the coating industry, polyurethane (PU) coatings exhibit excellent abrasion resistance, toughness and low temperature flexibility. Notably, the two-package solvent-borne PU coatings have a reputation for high performance even if they are cured at room

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temperature, and also provide excellent adhesion, chemical resistance, and abrasion resistance [15–18]. Most of non-degradable PU resins are insoluble and do not polish or erode immersed in sea water, which make them unsuitable for antifouling. Nevertheless, the traditional degradable PU films, with poor mechanical properties, can polish or erode after immersion in sea water. Therefore, cross-linkable degradable PU resins may solve this problem [19,20]. To meet these demanding requirements for marine antifouling, the degradable PU based on star-shaped polyester polyols could be introduced. The star-shaped polymers consist of at least three linear polymeric chains of comparable lengths radiating from one single multifunctional branched point [21–25]. The main feature of star-shaped polymers, different from the linear analogues of identical molar masses (Mn), is their compact structure increase in the crosslinking reactivity with polyisocyanate and improvement in film toughness [26,27]. However, reports on the application of star-shaped polyester polyols to coatings, particularly to two-component polyurethane antifouling coatings have been scarce.

In the present study, a series of star-shaped polyester polyols were synthesized by polycondensation reaction using initiators (trimethylolpropane or pentaerythritol) and  $\epsilon$ -caprolactone (CL). The degradable polyurethane (PU) films were prepared by mixing star-shaped polyester polyols and crosslinker agent (hexamethylene diisocyanate trimer). The number of hydroxyl of initiator and the average molecular weight of PCL chain in the star-shaped polyester polyols were specially investigated. The properties of polyurethane films based on star-shaped polyester polyols and their use for two-component antifouling coatings are reported in this paper.

## 2. Materials and methods

### 2.1. Materials

Trimethylolpropane (TMP) from Xiya Chemical Reagent Co., Ltd. was used as received without further purification. Pentaerythritol (PER) was from Tianjin Guangfu fine Chemical Research Institute. Stannous octoate ( $\text{Sn}(\text{Oct})_2$ ) was from Sinopharm Chemical Reagent Co., Ltd.  $\epsilon$ -Caprolactone (CL) (Aladdin) was distilled over  $\text{CaH}_2$  before use. Hexamethylene diisocyanate trimer (N3390 [NCO] =  $19.5 \pm 0.3\%$ ) was from Bayer materials science and technology (China) Co., Ltd. Jotacote Universal (a two-pack, abrasion resistant, high solids polyamine cured pure epoxy based primer coat) was from Jotun paint (China) Co., Ltd. Artificial sea water (pH 8.1) was prepared by mixing NaCl (23 g/L),  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (9.8 g/L),  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  (8.9 g/L), and  $\text{CaCl}_2$  (1.2 g/L). Cuprous oxide, zinc oxide, copper pyrithione and butyl acetate were of industry grade. All other reagents were of analytical grade without further purification.

### 2.2. Measurements

#### 2.2.1. Molecular weight measurements

The prepared star-shaped polyester polyols were characterized for molecular weight using gel-permeation chromatography (GPC).

The GPC experiments were performed using PL-GPC 50 Plus system (Agilent Technologies) consisting of refractive index detector and dual angle LS detector, and a set of PLgel columns (two identical PLgel (5  $\mu\text{m}$  MIXED-C) and one other PLgel (5  $\mu\text{m}$  Guard)). The prepared star-shaped polyester polyols were dissolved in HPLC grade tetrahydrofuran (THF) (1–1.5 mg/mL). Sample injection volume was 300  $\mu\text{L}$ , and the flow rate of carrier solvent (THF) was 1.00 ml/min at 39 °C. Polystyrene of known molecular weights was used as calibration standard. The number average molecular weight and polydispersity index were determined by software Cirrus GPC.

#### 2.2.2. Nuclear magnetic resonance spectroscopy

$^1\text{H}$  NMR spectra of the prepared star-shaped polyester polyols dissolved in  $\text{CDCl}_3$  (10–15 mg/mL) were acquired on a Bruker V-400 M model (400 MHz) using tetramethylsilane (TMS) as an internal standard.

#### 2.2.3. Fourier transform infrared spectroscopy

FTIR spectra of the prepared star-shaped polyester polyols were recorded in transmission mode on KBr pellets with a Fisher Nicolet iS 10 IR instrument. The frequency range was from 4000 to 500  $\text{cm}^{-1}$  with average of 32 scans at a resolution of 4  $\text{cm}^{-1}$ . Additionally, FTIR spectra of the dry PU films were directly recorded in ATR mode with a Fisher Nicolet iS 10 IR instrument. The frequency range was from 4000 to 700  $\text{cm}^{-1}$  with average of 64 scans at a resolution of 4  $\text{cm}^{-1}$ .

#### 2.2.4. Thermal analysis

The Tg values of PU films were measured using DSC instruments (DSC 1, Mettler). Samples (5–10 mg) were equilibrated against ambient temperature and humidity prior to measurement. Measurements were made under a nitrogen atmosphere. Samples were heated in the first run to 160 °C, then cooled to –60 °C and heated in a second scan to 160 °C at 10 °C/min. The Tg values of PU films were determined from the second heating scan by the half Cp extrapolated tangent method.

#### 2.2.5. X-ray diffraction

X-ray diffraction (XRD) measurements of PU films were carried out with a XRD instrument (Empyrean, PANalytical). The 2 $\theta$  scanning rate was 4°/min and scanning range was 10–30°.

### 2.3. Synthesis of star-shaped polyester polyols

The star-shaped polyester polyols were synthesized by polycondensation reaction using CL and initiator (TMP or PER) shown in Table 1 and Scheme 1. The lengths of the poly( $\epsilon$ -caprolactone) (PCL) arms were varied by controlling the molar ratios of CL/initiating hydroxyl group molar ( $[\text{CL}]_0/[\text{—OH}]_0$ ). Varying the different ratios of  $[\text{CL}]_0/[\text{—OH}]_0$ , a series of star-shaped polyester polyols were synthesized. The star-shaped polyester polyols were named as TMP/CL<sub>3</sub>, TMP/CL<sub>6</sub>, TMP/CL<sub>9</sub>, TMP/CL<sub>12</sub>, TMP/CL<sub>15</sub>, and PER/CL<sub>12</sub> in reference to the components used. The polycondensation reactions were performed in a four-necked reaction kettle equipped nitrogen purging device, and Dean-Stark trap. The CL, initiator (TMP or PER),

**Table 1**  
Synthesis of star-shaped polyester polyols.

Samples	TMP (mol)	PER (mol)	CL (mol)	$[\text{CL}]_0/[\text{—OH}]_0$	$[\text{CL}]/[\text{—OH}]$ (NMR)	Mn (NMR)	Mn (GPC)	Mw/Mn (GPC)	Viscosity (cP)	Yield (%)
TMP/CL <sub>3</sub>	0.1	–	0.3	1	1.47	636	426	1.137	1765	95.43
TMP/CL <sub>6</sub>	0.1	–	0.6	2	2.34	934	714	1.256	1943	95.78
TMP/CL <sub>9</sub>	0.1	–	0.9	3	3.36	1283	992	1.195	2043	96.42
TMP/CL <sub>12</sub>	0.1	–	1.2	4	4.64	1720	1398	1.215	2143	96.57
TMP/CL <sub>15</sub>	0.1	–	1.5	5	5.58	2042	1692	1.246	2196	96.65
PER/CL <sub>12</sub>	–	0.1	1.2	3	3.75	1846	1309	1.143	2093	96.43

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